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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to zeolite membrane used for eye cluster ******, a molecule sieve, etc., for example, and a synthesizing method for the same by having the network structure of the diameter fine pores of uniform.
[0002]
[Description of the Prior Art]Zeolite consists of a skeleton of crystalline aluminosilicate, and the crystal structure has the network structure of the diameter fine pores of uniform with minute molecular size of several to about ten A, and the size and the network structure of the fine pores change with kinds of zeolite.
[0003]For this reason, zeolite can shut up the molecule of a specific size, or it can stick to it, and the molecule sieve which carries out the sieve division of the molecule with a size using this character, and a cluster shut it up, and it is used as a catalyst etc.
[0004]The crystal powder of this zeolite as a silica source a sodium silicate, colloidal silica, etc., The hydration gel of an alkali aluminosilicate is prepared using sodium aluminate, aluminium hydroxide, etc. as an alumina source, and it is compounded by the hydrothermal crystallization method crystallized under existence of high temperature high pressure water by using this hydration gel as a raw material.
[0005]On the other hand, the trial which compounds film-like zeolite immerses a porous substrate in the solution of the same raw material as the case of the hydrothermal crystallization method of the above-mentioned zeolite powder, it carries out with the hydrothermal crystallization method which crystallizes this under existence of high temperature high pressure water in accordance with a hydrothermal crystallization method, and the polycrystal membrane of zeolite is obtained. For example, having compounded A type zeolite membrane with the hydrothermal crystallization method using the porosity alumina substrate is reported in the collection 2 of the Society of Chemical Engineers, Japan autumn convention research presentation lecture gists, the 99th page, and 1993.
[0006]In the collection 1 of the Society of Chemical Engineers, Japan autumn convention research presentation lecture gists, the 121st page, and 1993. It is made to dry after applying to an alumina buck the aluminosilicate sol prepared using a sodium silicate solution, sulfuric anhydride aluminum, and sulfuric acid, It is indicated by by keeping at 448K in triethylamine, ethylenediamine, and the steamy atmosphere of water that the mix crystal film of ZSM-5 and a ferrierite which is one sort of zeolite was obtained.
[0007]

[Problem(s) to be Solved by the Invention]Although each zeolite membrane obtained by these methods is precise polycrystal membrane, the zeolite membrane which carried out orientation to specific crystal orientation is the actual condition which is not yet compounded. However, to use zeolite membrane for eye cluster ******, it is required for the crystal orientation of one way to have gathered at least.

[0008]An object of this invention is to provide the precise zeolite membrane which carried out orientation to specific crystal orientation in view of this conventional situation.

[0009]

[Means for Solving the Problem]In order to attain the above-mentioned purpose, zeolite membrane which this invention provides is the zeolite membrane which it was formed on a monocrystal substrate of an oxide, a semiconductor, or metal, and gave priority to and carried out orientation to specific crystal orientation.

[0010]A synthesizing method of zeolite membrane of this invention forms zeolite membrane which gave priority to and carried out orientation to specific crystal orientation by applying raw material sol containing a zeolite composing element on a monocrystal substrate of an oxide, a semiconductor, or metal, and making it crystallize by heat treatment in atmosphere containing a steam.

[0011]

[Function]In this invention, it became compoundable [the precise zeolite membrane which carried out orientation to crystal orientation specific on the substrate] by using as a substrate the monocrystal substrate which consists of either an oxide, a semiconductor and metal. Sapphire, crystal, magnesium oxide, etc. can be used in an oxide, silicon, gallium arsenide, etc. can be used with a semiconductor, and gold, nickel, copper, etc. can be used with metal as a material of a monocrystal substrate.

[0012]After composition of the stacking tendency zeolite membrane of this invention applies the raw material sol containing a zeolite composing element and dries and gels on the monocrystal substrate of the above-mentioned oxide, a semiconductor, or metal using a sol gel process, it is based on the method of crystallizing by heat treatment. It is preferred to use the aluminosilicate sol prepared by hydrolysis of the alkoxide as raw material sol which contains a zeolite composing element especially.

[0013]The classic example of the synthesizing method of the stacking tendency zeolite membrane by this invention method is shown. First, each alkoxide of silicon, aluminum, and an alkaline metal which is a zeolite composing element is dissolved in alcohol used as a solvent, it is considered as an alcohol solution, and raw material sol is obtained by addition of water or hydrolysis by the moisture in the atmosphere, and polymerization.

[0014]If the alkoxide to be used is an alkoxide of a zeolite composing element, it may be arbitrary, for example, a tetraethoxysilane, a tetramethoxy silane, etc. can be used for it as an alkoxide of silicon. Some of silicon, aluminum, and the alkaline metals may use the hydroxide instead of an alkoxide. Not using an alkoxide, mineral salt which is used with a hydrothermal crystallization method can be used, and the raw material sol containing a zeolite composing element can also be prepared.

[0015]Next, the prepared raw material sol is applied to a monocrystal substrate like the above. In the conventional hydrothermal crystallization method, since the mole ratio of the water in hydration gel was restricted within the limits of the specification which changes with kinds of zeolite, the viscosity control of gel was difficult for it, but. Since it is changed comparatively freely with the quantity of the alcohol which applies the viscosity of sol by this invention method, or water, it is possible to be able to apply on a substrate using a spin coat, dip coating, etc., and to form the film of arbitrary thickness simply and uniformly moreover.

[0016]It crystallizes by heat-treating in the atmosphere which remains as it is as for the raw material sol applied to the substrate, or contains a steam after drying at the temperature of 100 ** or less in the atmosphere, and the zeolite membrane of a stacking tendency is formed on a substrate. Zeolite, such as A type, an X type, and Y type, is compoundable at the temperature of 200 ** or less, and synthetic time may be so short that temperature is high.

[0017]What is necessary is just to heat using an electric furnace etc., after putting water in a container, installing a substrate on a buck as a method of heat-treating in the atmosphere containing a steam so that a substrate and water may not contact, and sealing the whole. The maximum vapor tension of the water in synthesizing temperature may be sufficient as the pressure in a container, and it is not necessary to pressurize it from the outside.

[0018]The zeolite membrane formed by this this invention method is precise, and it has the stacking tendency which was influenced by the crystal orientation of a monocrystal substrate, and gave priority to and carried out orientation to specific crystal orientation according to the used monocrystal substrate. Although the zeolite membrane obtained is usually polycrystal, it is also possible by choosing a suitable monocrystal substrate and raw material to compound the zeolite membrane of a single crystal.

[0019]In forming zeolite membrane with the conventional hydrothermal crystallization method, although it needed to be made for a specific element to become superfluous to the target zeolite presentation, the mole ratio in the hydration gel of a raw material, By this invention method, the mole ratio of the zeolite composing element in raw material sol presupposes that a raw material is the same as that of the target zeolite presentation irrespective of an alkoxide or mineral salt. Therefore, while preparation of raw material sol is easy, zeolite can be obtained with the greatest yield.

[0020]

[Example]

It mixed to 20 ml of methanol which is [which is 1.46 g of tetraethoxysilanes as a source of example 1 silicon] 1.72 g of tri-sec-butoxyaluminum as an aluminum source and which is a solvent about the methoxy sodium 0.38g as a sodium source.

[0021]Raw material sol was prepared by adding 5 ml of water to the obtained solution, and making it hydrolyze and polymerize [be / it / under / air / setting] at a room temperature. The oxide mole ratios in raw material sol are SiO_2/aluminum$_2O_3$=2.0 and Na_2O/SiO_2=0.5.

[0022]Next, raw material sol was applied with the spin coat on the single crystal sapphire C side board, into the atmosphere, it was made to dry at 95 ** and dry gel was formed. This dry gel was laid on the buck in glass reaction vessels the whole substrate, water was put in and sealed to the reaction vessel, and it heated at 100 ** for 3 hours using the electric furnace.

[0023]It was checked that the film formed on the substrate has a crystal structure of A type zeolite according to an X diffraction. When the section of this film was observed by SEM, it became clear that it was a very precise structure.

[0024]It receives, although the peak intensity ratio of the diffraction line (200) of the X diffraction of A type zeolite powder and a diffraction line (220) is 2:1, In A type zeolite membrane obtained by this example, carrying out priority orientation so that the same peak intensity ratio may be 10:1 and the field (100) of a zeolite crystal may become parallel to a substrates face was checked.

[0025]After applying the raw material sol prepared like example 2 Example 1 with a spin coat on a single

crystal crystal (001) side board, desiccation and heat treatment were performed like Example 1. It was checked that the film formed on the substrate has a crystal structure of A type zeolite according to an X diffraction. When the section of this film was observed by SEM, it became clear that it was a very precise structure.

[0026]It receives, although the peak intensity ratio of the diffraction line (200) of the X diffraction of A type zeolite powder and a diffraction line (220) is 2:1, In A type zeolite membrane obtained by this example, carrying out priority orientation so that the same peak intensity ratio may be 8:1 and the field (100) of a zeolite crystal may become parallel to a substrates face was checked.

[0027]After applying the raw material sol prepared like example 3 Example 1 with a spin coat on a nickel single crystal (100) side board, desiccation and heat treatment were performed like Example 1. It was checked that the film formed on the substrate has a crystal structure of A type zeolite according to an X diffraction. When the section of this film was observed by SEM, it became clear that it was a very precise structure.

[0028]It receives, although the peak intensity ratio of the diffraction line (200) of the X diffraction of A type zeolite powder and a diffraction line (220) is 2:1, In A type zeolite membrane obtained by this example, carrying out priority orientation so that the same peak intensity ratio may be 7:1 and the field (100) of a zeolite crystal may become parallel to a substrates face was checked.

[0029]After applying the raw material sol prepared like example 4 Example 1 with a spin coat on a silicon single crystal (100) side board, desiccation and heat treatment were performed like Example 1. It was checked that the film formed on the substrate has a crystal structure of A type zeolite according to an X diffraction. When the section of this film was observed by SEM, it became clear that it was a very precise structure.

[0030]It receives, although the peak intensity ratio of the diffraction line (200) of the X diffraction of A type zeolite powder and a diffraction line (220) is 2:1, In A type zeolite membrane obtained by this example, carrying out priority orientation so that the same peak intensity ratio may be 7.5:1 and the field (100) of a zeolite crystal may become parallel to a substrates face was checked.

[0031]It mixed to 20 ml of methanol which is [which is 2.33 g of tetraethoxysilanes as a source of example 5 silicon] 0.98 g of tri-sec-butoxyaluminum as an aluminum source and which is a solvent about the methoxy sodium 0.22g as a sodium source.

[0032]Raw material sol was prepared by adding 5 ml of water to the obtained solution, and making it hydrolyze and polymerize [be / it / under / air / setting] at a room temperature. The oxide mole ratios in raw material sol are SiO_2/aluminum$_2O_3$=5.6 and Na_2O/SiO_2=0.18.

[0033]Next, applied the above-mentioned raw material sol with the spin coat on the single crystal sapphire C side board, it was made to dry at 95 ** in the atmosphere, and dry gel was formed. This dry gel was laid on the buck in glass reaction vessels the whole substrate, water was put in and sealed to the reaction vessel, and it heated at 100 ** for 3 hours using the electric furnace.

[0034]It was checked that the film formed on the substrate has a crystal structure of Y type zeolite according to an X diffraction. When the section of this film was observed by SEM, it became clear that it was a very precise structure.

[0035]It receives, although the peak intensity ratio of the diffraction line (111) of the X diffraction of Y type zeolite powder and a diffraction line (120) is 25:1, In Y type zeolite membrane obtained by this example,

carrying out priority orientation so that the same peak intensity ratio may be 1:5 and the field (100) of a zeolite crystal may become parallel to a substrates face was checked.

[0036]0.5 g of aluminium hydroxide was used as the sodium silicate 1.05g which contains 36.5% of the weight of SiO_2, and 18% of the weight of Na_2O as a source of example 6 KEISO, and an aluminum source, 0.01 g of sodium hydroxide and 20 ml of water were used as a sodium source, and raw material sol was prepared. The oxide mole ratios in raw material sol are SiO_2/aluminum$_2O_3$=2.0 and Na_2O/SiO_2=0.5.

[0037]Next, this raw material sol was applied with the spin coat on the single crystal sapphire C side board, and was dried and heat-treated like Example 1. It was checked that the film formed on the substrate has a crystal structure of A type zeolite according to an X diffraction. When the section of this film was observed by SEM, it became clear that it was a very precise structure.

[0038]As opposed to the peak intensity ratio of the diffraction line (200) of the X diffraction of A type zeolite powder and a diffraction line (220) being 2:1, In A type zeolite membrane obtained by this example, carrying out priority orientation so that the same peak intensity ratio may be 10:1 and the field (100) of a zeolite crystal may become parallel to a substrates face was checked.

[0039]The raw material sol prepared like the comparative example example 1 was applied with the spin coat on the polycrystalline alumina board, and desiccation and heat treatment were carried out like Example 1.

[0040]Although having a crystal structure of A type zeolite according to an X diffraction was checked, orientation of the film formed on the substrate had not been carried out to specific crystal orientation. When the section of this film was observed by SEM, it became clear that the macro pore of a large number whose paths are 0.1-several micrometers existed in a film.

[0041]

[Effect of the Invention]According to this invention, the precise zeolite membrane which carried out orientation to specific crystal orientation can be formed on a monocrystal substrate, and the zeolite membrane which can be used for eye cluster ****** etc. can be provided.

[Translation done.]